Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 593-595

Characterization of Charged Traps near Si-SiO_2 Interface in Photo-CVD SiO_2 Film

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Charged traps near the Si-SiO_2 interface in the SiO_2 films deposited by photo-induced chemical vapor deposition (photo-CVD) have been analyzed by photo I-V method. Positively charged traps decrease monotonously in the region between 20Å and 100Å from the Si-SiO_2 interface to the inside in the as-deposited film. The traps between 20Å and 40Å are relaxed by annealing, and the traps between 40Å and 100Å are decreased by annealing in O_2. Furthermore the results of electron spin resonance (ESR) suggest the possibility that the positively charged traps (20-40Å) correspond to the defects observed in ESR spectra.

1. Introduction

Good quality SiO_2 films can be prepared at low temperature by photo-induced chemical vapor deposition (photo-CVD),[1,2] but detailed information of traps in them is not clear. Traps in oxide films affect on properties of metal oxide semiconductor (MOS) devices, so it is important to clear the characteristics of traps and decrease them for application to ultra large integration (ULSI) or very large integration (VLSI) devices. In this paper, we have clarified spatial distribution of charged traps in photo-CVD SiO_2, especially near the Si-SiO_2 interface, by photo I-V method,[3] and discussed structure of the charged traps with the assistance of electron spin resonance (ESR).

2. Sample preparation and theory of photo I-V method

(100) n-type Si with resistivity of 0.01-0.02Ωcm was used as a sample in photo I-V measurement. It was cleaned by RCA method and etched by 1% HF before deposition. SiO_2 films of 3000Å thickness were deposited on Si substrates at 300°C by photo-CVD using Si_2H_6 and O_2. The growth and annealing conditions are shown in Table I. Electrode films are Au as a semitransparent electrode at the SiO_2 side, AuSb as a electrode at the Si side, and Al as a contact pad on Au.

Using this MOS structure, characteristics of the photocurrent were caused under voltage application by photoinjection of electrons from Si into SiO_2 under ultra violet (UV) light of 5.3eV of Xe lamp. The theoretical photocurrent voltage dependence considering the barrier lowering and scattering of electrons[4] is expressed as

$$I = I_0 \exp\left(-\frac{x_0}{\ell}\right) \tag{1}$$

$$I_0 = A(h\nu - \Phi_1 + \Delta\Phi)^2 \tag{2}$$

Table I. Growth and annealing conditions

Substrate	
silicon, n-type, (100),	
0.01-0.02 Ωcm (Photo I-V)	
1000-2000 Ωcm (ESR)	
Photo-CVD SiO_2 film	
Gas flow ratio of Si_2H_6 / O_2 :	0.36
VUV light source :	D_2 lamp
Growth temp. :	300°C
Working pressure :	23.3Pa
Thickness :	~3000Å (Photo I-V)
	~5000Å (ESR)
Annealing	
500°C, 1hour, N_2 or O_2	

$$x_0 = \sqrt{\frac{qd}{16\pi\varepsilon_i(Vg + \Phi_1 - \Phi_2)}} \tag{3}$$

$$\Delta\Phi = \frac{2q}{16\pi\varepsilon_i x_0} \tag{4}$$

where ℓ is the scattering length of electrons, d is the insulator thickness, ε_i is the high-frequency dielectric constant, Vg is the applied voltage, Φ_1 and Φ_2 are the barrier energies at the two insulator interfaces, $h\nu$ is the photon energy, and A is a constant for a given light intensity and photon energy.[5]

The spatial distribution of the charged traps in the oxide film can be obtained from the voltage shift in photo I-V curves before and after irradiation with UV light.[3] An example of the voltage shift in photo I-V curves is shown in Fig.1. Density of the charged traps $\rho(x_0)$ is written as

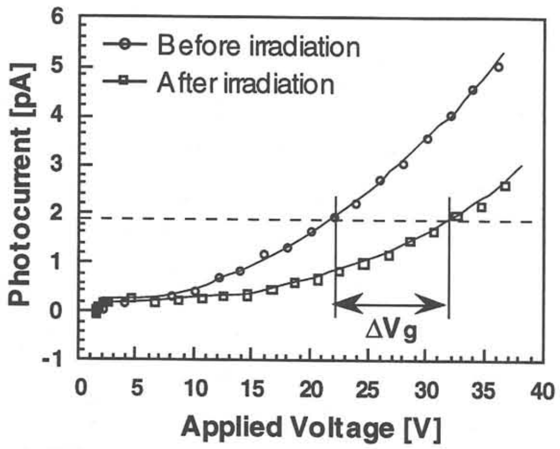


Fig. 1. Example of the voltage shift in photo I-V curves before and after irradiation with UV light.

$$\frac{d\Delta V_g}{dx_0}=\frac{d}{\varepsilon_{ox}}\rho(x_0) \qquad (5)$$

where ε_{ox} is the low-frequency dielectric constant of the insulator .

3. Results and discussions

3.1. Photo I-V measurements

Figure 2 (a) shows the experimental photo I-V curve of the as-deposited sample after neutralized by irradiation with UV light of 3.8eV for 3 hours. Open circles are experimental data and solid line is the theoretical curve obtained from the equations (1)-(4). The experimental data are in good agreement with the theoretical curve which is calculated by assuming scattering length ℓ of 6Å. Photo I-V curves of the samples annealed in N_2 and in O_2 are shown in figure 2 (b). The scattering length of the N_2-annealed sample is 8Å and it is almost equal to that of the as-deposited one. However, the scattering length of the O_2-annealed sample is 35Å and much larger than those of the as-deposited and N_2-annealed ones. Scattering length is considered to be a parameter of the electronic structure of the region near the injected interface in the oxide, so the structural defects in the region near the Si-SiO_2 interface in the photo-CVD SiO_2 film can be decreased by annealing in O_2.

Figure 3 shows the charged trap distributions between about 20Å and 100Å from the Si-SiO_2 interface in the photo-CVD SiO_2 films which are as-deposited, annealed in N_2 and annealed in O_2. Positively charged traps decrease monotonously from the Si-SiO_2 interface to the inside in the as-deposited film. The traps between about 20Å and 40Å are decreased by annealing either in N_2 or O_2, and the traps between about 40Å and 100Å are decreased only by annealing in O_2. It is considered that the traps (20-40Å) are attributable to the defects relaxed by the thermal effect and the traps (40-100Å) are related to oxygen-deficient defects. The distribution and amount of the traps in the photo-CVD SiO_2 film after annealing in O_2 are approximately equal to those of the SiO_2 film oxidized thermally at 1000°C as shown in Fig. 4.

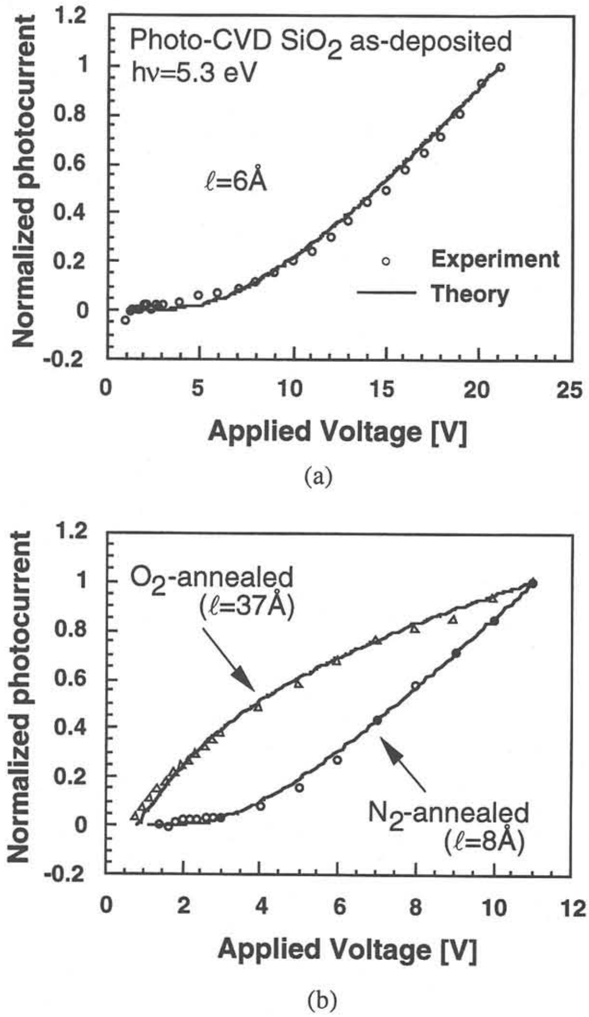
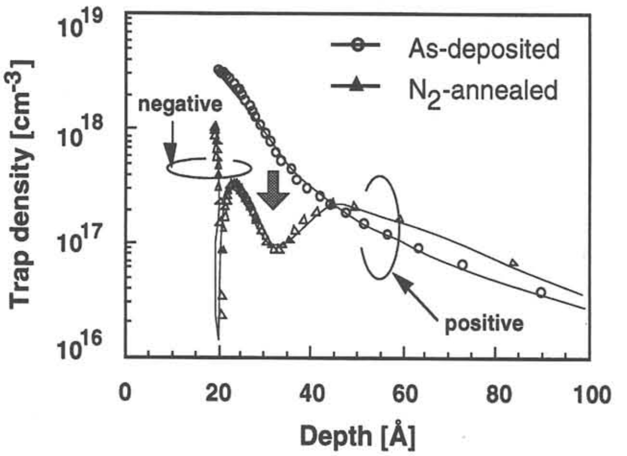


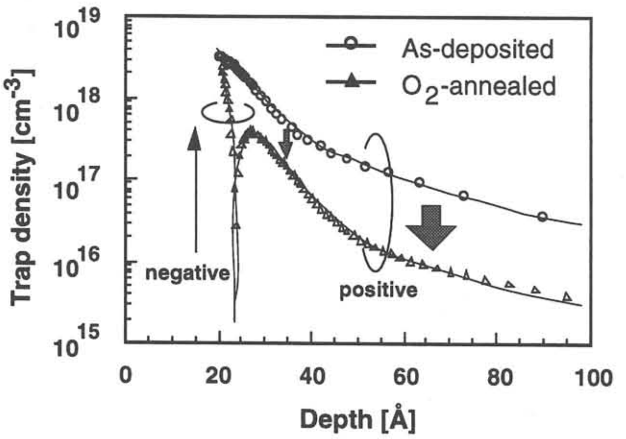
Fig. 2. Experimental data and theoretical curves of photo I-V characteristics induced by photoinjection from Si into SiO_2 for (a) as-deposited film and (b) films annealed in N_2 or in O_2.

3.2. ESR measurements

(100) n-type Si with resistivity of 1000-2000Ωcm was used to measure defects having unpaired electron. SiO_2 films of 5000Å were deposited by photo-CVD under the conditions in Table I. Figure 5 shows ESR spectra of as-deposited film, films annealed in N_2 and in O_2 and film irradiated with UV light for 3 hours. Two peaks can be observed at $g \approx 2.0000$ and $g \approx 2.0200$ in the spectrum of the as-deposited sample (trace A), and these intensities are independent of the measurments angle. The peak at $g \approx 2.0000$ seems to be due to the resonance of the E'-center. These peaks disappear in the spectra of the samples annealed in N_2 and in O_2 (trace B and C). Furthermore, the peaks in the as-deposited film are reduced by irradiation with UV light (trace D); the positively charged traps are neutralized by excitation of electrons. Assuming this model, the positively charged traps obtained from photo I-V method, existing between 20Å and 40Å from the Si-SiO_2 interface, are considered to be related to the defects detected in ESR. But, detailed analysis is needed to clarify the origin.



(a)



(b)

Fig. 3. Spatial distributions of the charged traps near the Si-SiO_2 interface in the photo-CVD SiO_2 films (a) before and after annealing in N_2 and (b) before and after annealing in O_2.

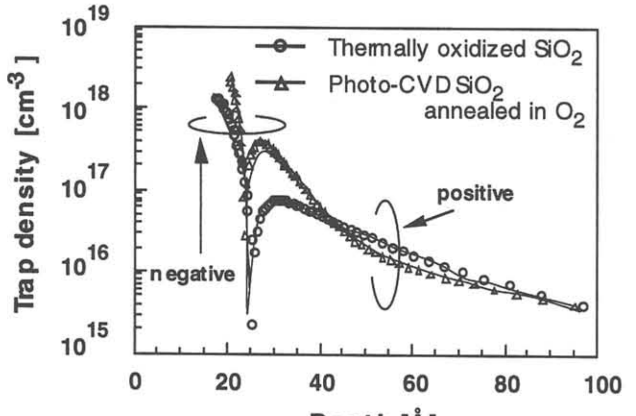


Fig. 4. Spatial distributions of the photo-CVD SiO_2 film annealed in O_2 and the thermally oxidized SiO_2 film

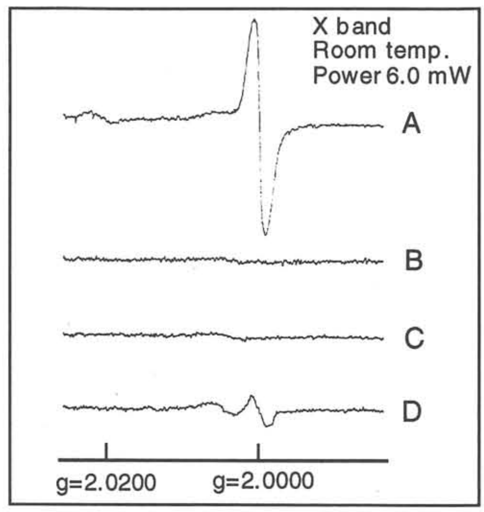


Fig. 5. ESR spectra of photo-CVD SiO_2 films. A: as-deposited, B: annealed in N_2, C: annealed in O_2, D: irradiated with UV light for 3 hours.

4. Conclusions

The characteristics of charged traps in photo-CVD SiO_2 film were discussed by photo I-V method and ESR measurments. The scattering lengths are obtained from photo I-V curves, and the electronic structure of the region near the Si-SiO_2 interface is improved by annealing in O_2. Positively charged traps distribute between about 20Å and 100Å from the Si-SiO_2 interface in the as-deposited film, and they monotonously decrease from the interface. The traps between about 20Å and 40Å are decreased by thermal annealing, and the traps between about 40Å and 100Å are decreased by annealing in O_2. Two peaks are observed in ESR spectrum of as-deposited film and diminished by thermal annealing and reduced by irradiation with UV light. Then the positively charged traps (20-40Å) obtained from photo I-V method and the defects detected by ESR measurments may be considered to be related each other. But, further investigations will be needed to clear it.

Acknowledgment

The authors wish to thank Dr. H. Okamoto, Dr. K. Hattori, Dr. K. Yamashita and Mr. C. Sada of Osaka University for their helpful discussions and technical assistance.

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